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# Synthesis, structure, and properties of a mononuclear ferrocenophane bearing two carbodiimide units as bridges

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ABSTRACT

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#### Introduction

Since ferrocene was discovered in 1951<sup>1</sup> a remarkable attention has been paid to this robust building block which can easily be functionalized by using most of the procedures known for organic synthesis. As a result, a wide variety of ferrocenebased molecules have been directly synthesized starting from the parent organometallic complex. On the other hand, the high stability of such ferrocene-based derivatives together with their easiness to reversibly undergo single electron oxidation to give stable ferrocenium radical cations makes ferrocenyl systems particularly attractive in many fields such as homogeneous catalysis, especially in stereoselective and asymmetric transformations, in electrochemistry, particularly in electrontransfer processes, as new materials, as anticancer reagents, etc.<sup>2</sup> The versatility of functionalization of ferrocene has opened the way to the rapid expansion of its chemistry including the preparation of bridged ferrocenes, called ferrocenophanes, which are ring systems in which the two cyclopentadienyl groups of ferrocene are linked by an atomic or a molecular bridge. Among the different classes of ferrocenophanes reported in the last decades particular attention have been paid to the families of [n]ferrocenophanes mononuclear and multinuclear [m.n]ferrocenophanes<sup>3</sup> due to their applications in molecular recognition and sensing,<sup>4</sup> or in the preparation of conjugated polymers via ring opening polymerization (ROP)<sup>5</sup> or ringopening metathesis polymerization (ROMP).6

A novel bis(carbodiimido)[11]ferrocenophane was synthesized using a methodology involving an aza, Wittig reaction of the 1,1'-bis(triphenylphosphoralydienamino)ferrocene with the commercially available 1,3-bis(2-isocyanatopropan-2-yl)benzene. Moreover, its electrochemical and chemical properties were also examined. The ureido derivative formed when the bis(carbodiimido)ferrocenophane was hydrolyzed under acidic conditions, behaves as a chemodosimeter for sensing nitrite anions in aqueous solutions

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Although the ferrocenophane chemistry has already acquired a high degree of maturity the synthesis of new types of these fascinating class of molecules is still of high interest. For this reason, and in a continuation of our ongoing studies involving the synthesis and structural characterization of new families of nitrogen-rich metallocenophanes with interesting structural, electrochemical and optical properties<sup>7</sup> we have now focused our research on the synthesis, characterization and electrochemical properties of the novel mononuclear [11]ferrocenophane **4** with the characteristic feature of having two carbodiimide functions as part of the ansa [11] bridge.

Despite the fact that the cyclic bis(carbodiimides) are extremely unstable compounds that undergo intramolecular [2+2] cycloadditions to give four-membered rings, such as 1,3-diazetidine-2,4-diimines,<sup>8</sup> it has also been reported that [3.3] ferrocenophane derivatives, in which the ferrocenyl termini are directly linked by two carbodiimide functions, can easily be derivatized to give extremely nitrogen-rich ferrocenophanes with unprecedented topologies.<sup>9</sup>

#### **Results and discussion**

A straightforward approach to **4** involves the use of the aza-Wittig methodology,<sup>10</sup> starting from the bis(iminophosphorane) **3**, readily prepared by the Staudinger reaction between triphenylphosphine and 1,1'-diazidoferrocene **2**.<sup>9c</sup> An advantage of this approach is that 1,1'-diazidoferrocene **2** is easily

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accessible from ferrocene by using 2,4,6triisopropylbenzenesulfonyl azide (trisyl azide) as a strong azidetransfer reagent.<sup>11</sup> Thus, reaction of 1,1'-dilithioferrocene with trisyl azide at 0° C afforded directly 2, which was used without further purification for the next step in the Staudinger reaction with triphenylphosphine. The aza-Wittig reaction of 3 with the commercially available 1,3-bis(2-isocyanatopropan-2-yl)benzene directly gave the bis(carbodiimido)[11]ferrocenophane 4, as the only reaction product, in 26% yield (Scheme 1),<sup>12</sup> which was fully characterized by using the standard spectroscopic tecniques (IR, <sup>1</sup>H- and <sup>13</sup>C-NMR,), mass spectrometry and elemental analysis as well as by single crystal X-ray diffraction.<sup>1</sup>



Scheme 1. Pathway followed for the preparation of ferrocenophane 4

Thus, the formation of the carbodiimide function is clearly evidenced by the appearance in the IR spectrum of a strong absorption band at  $\tilde{v} = 2125$  cm<sup>-1</sup>. Moreover, its <sup>1</sup>H NMR spectrum shows, in addition to the singlet associated to the protons present in the four methyl groups, two different pseudotriplets, corresponding to the  $H_{\alpha}$  and  $H_{\beta}$  present in the Cp units belonging to the ferrocene moiety. However, a characteristic feature of this <sup>1</sup>H NMR spectrum is the appearance of a different pattern for the aromatic signals, depending on the deuterated solvent used. Thus, by using CD<sub>3</sub>CN two different singlets at  $\delta = 7.43$  ppm and  $\delta = 8.23$  ppm, integrating three protons and one proton respectively, were observed. However, the <sup>1</sup>H NMR spectrum carried out in CDCl<sub>3</sub>, showed a set of four different signals for the magnetically different aromatic protons (H2, H5, and H4/H6) present in 4. This pattern of signals (Figure 1), typical for an AMNN' system, fully agrees with that of a simulated model compound<sup>14</sup> (see Electronic Supplementary Information ESI, Figure SI 2) similar to 4, in which the ferrocene and *m*-xylylene units are directly linked by cabodiimide groups. On the other hand, the <sup>13</sup>C NMR spectrum is also in agreement with the structure proposed for 4.



# **Figure 1.** Pattern of signals observed in the aliphatic and aromatic region of the <sup>1</sup>H NMR of **4**, in CDCl<sub>3</sub>.

The structure of compound 4 has been also resolved by single crystal X-ray diffraction (Figure 2 up; see also ESI). Compound 4 crystallizes as an orange prism in the orthorhombic space group P  $2_12_12_1$  with one molecule in the asymmetric unit. The two cyclopentadienyl (Cp) rings of the ferrocenyl moiety are perfectly planar (the mean deviation from planes being 0.0027 and 0.0041 Å). The Cp rings are twisted from the eclipsed conformation, the average torsion angle C1-centroid(Cp)<sub>1</sub>centroid(Cp)<sub>2</sub>-C10 being 27.55° and have an almost parallel orientation with a tilt angle of 1.2°. The organic ligand is attached to the C1 and C6 carbon atoms of the Cp rings through the carbodiimide groups-N1=C11=N2- and -N3=C12=N4-, respectively. The distances and angles of the carbodiimides are: 1.219(2) and 1.2215(19) Å and 170.73(15)° (N1-carbodiimide) and 1.237(2) and 1.206(2) Å and 169.67(15)° (N3-carbodiimide). The average torsion angle N1-centroid(Cp)<sub>1</sub>-centroid(Cp)<sub>2</sub>-N3 is 102.15° and the benzene ring of the ligand is rotated respect to the Cp rings, the angle between mean planes being 118.2 (C1ring) and 118.5° (C6-ring).

Regarding the crystal structure of **4**, molecules are interlinked by intermolecular C-H··· $\pi$  interactions between the H23C hydrogen atom and the benzene ring of the organic ligand of a neighbouring molecule. The distance between the hydrogen and the centroid of the ring is 2.807 Å. The result of these interactions is the formation of infinite chains along the *a*-axis. These chains are arranged in planes perpendicular to the *b*-axis in a way that the chains of adjacent planes exhibit opposite directions (Figure 2, down).





Figure 2. Crystal structure of compound 4 (ORTEP molecular representation and atom-labelling scheme)(up), and crystal packing diagram of 4 (down).

The electrochemical behavior of ferrocenophane **4** was studied by cyclic voltammetry (CV), and Osteryoung square-wave voltammetry (OSWV) in solutions of CH<sub>3</sub>CN (c = 5 x 10<sup>-4</sup> M) containing 0.1 M of  $[(n-Bu)_4N]PF_6$  (TBAHP) as supporting electrolyte. As expected, the CV of **4** shows a reversible oneelectron oxidation wave at  $E_{1/2} = 450$  mV versus decamethylferrocene (DCMF) (Figure 3). The criteria applied for reversibility was a separation of 60 mV between cathodic and anodic peaks, a ratio for the intensities of the cathodic and anodic currents I<sub>c</sub>/I<sub>a</sub> of 1.0, and no shift of the half wave potentials with varying scan rates. Of course, the magnitude of this  $E_{1/2}$  is identical as that obtained from the corresponding OSWV peak (Figure SI 6).



**Figure 3.** CV of **4** (5 x  $10^{-4}$  M) in CH<sub>3</sub>CN with TBAHP (0.1 M) as supporting electrolyte, scanned at 0.1 V.s<sup>-1</sup>. Decamethylferrocene was used as an internal standard

An interesting point in carbodiimide chemistry include their hydrolysis to give the corresponding urea functions, which, in turn, can be used as H-bond donors in a variety of anion receptors.<sup>15</sup> Therefore, we decided to explore the possibility of converting the bis-carbodiimidophane **4** into a new kind of very preorganized ferrocenophane receptor **5**, bearing in its molecule a ferrocene signaling unit directly attached to two urea binding sites for anions.

It is very well known that the hydrolysis of carbodiimides is a relatively slow reaction. However, it can be catalyzed by under acidic conditions.<sup>16</sup> Thus, while treatment of 4 under neutral conditions did not lead to any change in the molecule, when the hydrolysis reaction was carried out in the presence of HCl a new deep green species was formed, showing in its IR spectrum two absorptions bands at  $\tilde{v} = 3290$  and  $\tilde{v} = 1663$  cm<sup>-1</sup> which could be attributable to the presence, in the new compound formed, of NH and C=O groups, respectively. However, the <sup>1</sup>H- and <sup>13</sup>C NMR spectra of such species could not be obtained because it shown paramagnetic character. Nevertheless, its high resolution mass spectrum gave a molecular ion peak at m/z = 460.1564 which is in agreement with the calculated for the urea derivative (m/z)450.1562) (Figure SI 7). From these results, seems to be clear that under such conditions the final urea product should be formed but, immediately, it is oxidized to form a stable ferrocinium salt. Similar results were also obtained when HBF<sub>4</sub> was used instead of HCl, but, in this case, a new very broad band at  $\tilde{v} = 1060 \text{ cm}^{-1}$  was also observed in the IR spectrum, which is characteristic of the tetrafluoroborate anion. To prove the above mentioned hypothesis the hydrolysis reaction was carried out under nitrogen atmosphere, but, interestingly, under such conditions no green species were detected. However, when the flask was opened and the solution was allowed to stand to the air, it immediately acquired a greenish hue. These experimental and spectroscopic results suggest that once the hydrolysis of the carbodiimide has taken place, the resulting urea undergoes a rapid oxidation of the ferrocene unit, by the action of the atmospheric oxygen, to form the stable ferrocinium salt.<sup>17</sup>



To provide support to the observed phenomena and insight into the proposed nature of the species **6**, formed under hydrolysis conditions, a set of electrochemical studies were performed. Remarkably, linear sweep voltammetric (LSV) studies carried out with **4** and **6** demonstrate a shift of the sigmoidal voltammetric wave, from the region of anodic currents to the region of cathodic currents, when passing from **4** to **6**. This particular behavior clearly indicates the different oxidation state of the iron atom present in the bis-cabodiimidoferrocenophane **4** (Fe<sup>2+</sup>) and in the bis-ureidoferrocenophane **6** (Fe<sup>3+</sup>), and constitutes an additional evidence for the structure of **5** (Figure 4)



**Figure 4.** LSV of **4** (solid line) and **6** (dashed line) ( $c = 5 \times 10^{-4}$  M in CH<sub>3</sub>CN, in each case) with TBAHP (0.1 M) as supporting electrolyte, obtained using a rotating disk electrode at 100 mV s<sup>-1</sup> and 1000 rpm

To further evaluate the practical applicability of 6 as a electrochemical probe for sensing reducing anions, titration experiments in the presence of anions such as  $NO_2^{-1}$ ,  $SO_3^{-2}$ , I or ascorbate, by using electrochemical and optical techniques, were carried out. Whereas negligible changes in the LSV voltammogram of **6** were observed upon addition of  $SO_3^{2-}$  and  $\Gamma$ , a significant modifications was observed upon addition of NO<sub>2</sub> or ascorbate anions, although they were dependent on the anion studied. Thus, rotating disk voltammetry studies carried out upon addition of substoichiometric amounts of sodium ascorbate (c = 2.5 x  $10^{-2}$  M in H<sub>2</sub>O) to a solution of **6** (c = 5 x  $10^{-4}$  M in CH<sub>3</sub>CN) show a significant shift of the sigmoidal voltammetric wave toward anodic currents, indicating that this anion only promotes the reduction of the ferrocinium salt 6. By contrast, the same experiments carried out upon addition of  $NO_2^-$  anions to 6, in the presence of 1µL of HBF4, showed a significant shift of the sigmoidal voltammetric wave toward more positive potentials,

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indicating the development of a binding process between the receptor 6 and this anion (Figure SI 8).

The above mentioned sensing properties of 6 toward sodium nitrite have also been studied by using absorption spectroscopy. The UV-vis of **6** shows three absorption bands at  $\lambda = 279, 434$ and 600 nm, the lowest energy band being responsible for the green color of the compound, when it is in solution. Interestingly, the results obtained upon addition of aqueous solutions of the anions under study confirm the electrochemical results previously shown in the sense that the most characteristic variations in the UV-vis spectrum of the receptor are promoted upon addition of nitrite anions (c =  $2.5 \times 10^{-2}$  M in H<sub>2</sub>O) to a solution of 6 (c =  $1 \times 10^{-4}$  M) in CH<sub>3</sub>CN. Such changes involved the disappearance of the aforementioned three bands and the simultaneous appearance of a new one at  $\lambda = 357$  nm (Figure 5). These facts are responsible for the change of color from deep green to yellow, which is perceptible to the naked-eye. From these titration data, a detection limit<sup>18</sup> of 1.2 x 10<sup>-5</sup> M was calculated (Figure SI 9).



**Figure 5.** Changes in the absorption spectra of **6** (black) ( $c = 1 \times 10^{-4}$  M in CH<sub>3</sub>CN), upon addition of NaNO<sub>2</sub> ( $c = 2.5 \times 10^{-2}$  M in H<sub>2</sub>O), from 0 to 1 equiv (deep purple); arrows indicate the absorptions than increase or decrease during the experiment. Inset: visual features observed upon addition of the NO<sub>2</sub><sup>-</sup> anion.

Unfortunately, all attempts to study, through <sup>1</sup>H NMR spectroscopy, the type of mechanism taking place in the interaction between **6** and the nitrite anion were unsuccessful because the resulting new species still remained paramagnetic. However, the ESI MS spectrum showed a peak at m/z = 518 indicating that two nitroso groups have been incorporated to the structure of **6**, probably through a *N*-nitrosation reaction of the urea functions<sup>19</sup> (Figure 6).



**Figure 6.** ESI MS spectrum of the species formed upon reaction of nitrite ions with a solution of **6**, containing  $1\mu l$  of HBF<sub>4</sub>, indicating the functionalization of the molecule with two NO groups.

Because the nitrite anion induces a chemical reaction giving rise to a new product, different from the starting material, with different optical properties, and allows the detection of the anion, the compound **6** could be considered as a useful chemodosimeter for the naked eye detection of nitrite anions, whose concentration in drinking water is object of strict regulation and should not exceed 65  $\mu$ M.<sup>20</sup> Interestingly, although the research on the development of different types of chemosensors for the selective and sensitive determination of nitrite anions is very active,<sup>21</sup> to the best of our knowledge, methods based on the chemodosimeter approach, using urea functions, have not been described.

In summary, we report herein the synthesis, characterization and redox properties of a novel and very stable [11]ferrocenophane with the structural peculiarity of heaving an ansa bridge linking the cyclopentadienyl rings of the ferrocene unit, featuring carbodiimide functions as bridging groups. Moreover, under acidic conditions, this compound is transformed into the corresponding bis-ureido ferrocenophane which is easily oxidized under such reaction conditions to give a ferrocinium salt which can be used as chemodosimeter for sensing nitrite anions in aqueous solutions.

#### Acknowledgments

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- 12. To a solution of 1,3-bis(2-isocyanatopropan-2-yl)benzene (0.066g, 0.27 mmol) in dry THF (10 ml), at room temperature and under  $1.1^{\circ}-bis(N$ nitrogen atmosphere, а solution of triphenylphosphoranylideneamino)ferrocene 3 (0.2 g, 0.27 mmol) in the same solvent (30 ml) was added. The reaction mixture was stirred at room temperature for 24 h and the solvent was removed under reduced pressure. The residue was chromatographed on a silica gel column using CH<sub>2</sub>Cl<sub>2</sub>/n-hexane (8:2) as eluent. Once the solvent was evaporated under vacuum, the resulting product was crystallized from CHCl<sub>3</sub>/diethyl ether (1:5) to give a yellow solid in 26% yield (0.030 g). Mp: 168-170 °C. IR: v cm<sup>-1</sup> 2125 (-N=C=N-). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ/ppm 1.72 (s, 12H), 4.06 (m, 8H), 7.35 (m, 3H), 8.19 (m, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ/ppm 31.4 (CH<sub>3</sub>), 61.9 (q), 62.5 (2xCH, Fc), 63.3 (2xCH, Fc), 97.4 (q, Fc), 122.6 (CH), 123.1 (CH), 128.4 (CH), 147.4 (q, N=C=N). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN): δ/ppm 1.74 (s, 12H), 4.02 (st, 4H), 4.07 (st, 4H), 7.43 (s, 3H), 8.23 (s, 1H). <sup>13</sup>C NMR (75 MHz, CD<sub>3</sub>CN): δ/ppm 31.6 (CH<sub>3</sub>), 62.4(q), 66.1 (2xCH, Fc), 67.3 (2xCH, Fc), 98.6 (q, Fc), 123.5 (CH), 124.4 CH), 129.7 (CH), 138.1 (q), 148.7 (q, N=C=N). MS (ESI) m/z (%) 424 (M<sup>+</sup>, 100). Anal. Calc for  $C_{24}H_{24}FeN_4$ : C, 67.93; H, 5.70; N, 13.20. Found; C, 67.64; H, 5.35; N, 12.93.
- Crystallographic data (excluding structure factors) for the structure 4 reported in this Letter have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 1440651. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0)1223-336033 or email:deposit@ccdc.cam.ac.uk)
- 14. The simulated <sup>1</sup>H NMR spectrum for the proposed bis(carbodiimido)ferrocenophane model, was achieved by using the software MestreNova 9.1.0, Mestrelab Research, chemistry software solutions; 2014 Mestrelab Research S. L.
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- 17. To a solution of 1,1'-bis[N<sub>3</sub>,N<sub>3</sub>-(α,α,α',α'-tetramethylxylylen)-N<sub>1</sub>,N<sub>1</sub>-carbodiiimido][11]ferrocenophane **4** (0.05 g, 0.12 mmol) in THF (5 ml) a solution of diluted HCl (10%, 2 ml) was added dropwise. As the acid addition progressed, a gradual change in the color of the solution, from yellow to deep green, was observed. The reaction was followed by TLC and, after completion, the resulting compound was extracted with ethyl acetate (20 ml). The organic phase was dried over anhydrous MgSO4 and the solvent was removed under reduced pressure to give a green solid which was crystallized from CH<sub>2</sub>Cl<sub>2</sub>/n-hexane (1:9) and identified as the ferrocinium salt **6** (0.025 g, 47%). Mp: 221-225 °C. IR: ṽ cm<sup>-1</sup> 3290 (NH), 1663 (C=O). HRMS (ESI, M<sup>+</sup> + 1] calcd for C<sub>24</sub>H<sub>28</sub>FeN<sub>4</sub>O<sub>2</sub> 460.1562; found: 460.1564.
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